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(71) Applicant *(for all designated States except US)*: KATALEUNA GMBH [DE/DE]; AM Haupttor, D-06263 Leuna (DE).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: ALBERS, Edwin, W. [US/US]; 596 Severn Road, Severna Park, MD 21146 (US). BURKHEAD, Harry, W., Jr. [US/US]; 5528 Willys Avenue, Baltimore, MD 21227 (US). MCDANIEL, J., Gary [US/US]; 108 Glenmore Court, Bel Air, MD 21014 (US).

(74) Agents: STEINER, Arthur, J. et al.; Lowe, Price, Leblanc & Becker, Suite 300, 99 Canal Center Plaza, Alexandria, VA 22314 (US).

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(54) Title: CATALYST COMPOSITION AND METHODS FOR USING AND PREPARING SAME

(57) Abstract

A catalyst composition for a catalyst that reduces the emissions of sulfur compounds from industrial processes is disclosed. This catalyst is a spheroidal particle comprised of a mixture of inorganic oxides with an inorganic binder, an organic binder, or a mixture of these binders. The preferred embodiment is a particle containing zinc titanate. Also disclosed is the catalysts application in both fluid bed and ebullating bed processes such as petroleum refinery fluid catalytic cracking units and utility company coal gasification units. Additionally there is disclosed processes for preparing this catalyst using spray drying techniques and beading and tumbling techniques.

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CATALYST COMPOSITION AND METHODS FOR USING AND PREPARING SAME

BACKGROUND OF THE INVENTION

1. **Field of the Invention**

This invention relates to fluidizable catalysts, methods for using the catalysts to reduce the emissions of sulfur compounds from industrial processes, and methods for preparing such catalysts. Specifically, this invention relates to the composition of a fluid catalyst for removing sulfur oxides ("SO_x") from emissions, methods for using this fluid catalyst to remove sulfur oxides from emissions, and methods for preparing this fluid catalyst.

2. **Description of the Background Art**

The processing or burning of any sulfur containing fossil fuel can result in the emission of sulfur-containing compounds, such as H_2S and SO_x, to the atmosphere. To comply with increasingly stringent environmental regulations, catalyst manufacturers and other researchers are continuously seeking catalysts, additives, and processes to reduce the emissions of sulfur compounds from industrial processes. Several methods of desulfurization are currently being used commercially. These methods include flue gas scrubbing as well as various fixed bed, ebullating bed, and fluid bed catalytic reaction processes. Some of these processes treat the flue gas just prior to the release of the gas to the atmosphere. Other processes are performed upstream of the emission release in order to prevent the undesired emission from occurring. The goal of any process is to reduce the emission of sulfur-containing compounds into the atmosphere.

Processes wherein sulfur-containing compounds are emitted often occur in a fluid bed or an ebullating bed. An example of a fluid bed process is a fluid cracking catalyst operation in a petroleum refinery wherein SO_x emissions are generated in the fluid cracking catalyst regenerator and released in its flue gas. An example of an ebullating bed process is catalyst operation used by utility companies for coal gasification wherein H_2S is generated and emitted from the flue gas or hot gas.

The fluid cracking catalyst process that is used in petroleum refining presents a particularly difficult challenge for emissions control because a catalyst must both "capture" the sulfur compounds as SO_x under fluid cracking catalyst regenerator conditions and "release" this sulfur as H_2S under fluid cracking catalyst stripper/reactor conditions. Few catalysts have been found that can accomplish this dual requirement effectively and/or economically without adversely effecting operation of the fluid cracking catalyst unit.

The industry is lacking a composition for a fluid catalyst for economically removing sulfur oxides (" SO_x") from emissions from a variety of industrial processes. Further, the industry lacks effective and economical methods for using a fluid catalyst to remove sulfur oxides from emissions, and methods for preparing such a fluid catalyst.

SUMMARY OF THE INVENTION

The invention includes a catalyst composition. The catalyst or catalyst composition consists essentially of at least one SO_x capturing oxide and at least one inorganic binder.

The invention also includes a process for reducing the amount of SO_x emissions passing through a fluid particle bed. This process comprises the step of introducing into the fluid particle bed a microspheroidal

catalyst having a composition comprising at least one SO_x capturing oxide and at least one inorganic binder. The next step is oxidizing on the microspheroidal catalyst SO_x emissions of SO_2 to SO_3 in a fluid particle bed regenerator. The step of capturing the SO_3 in the fluid particle bed regenerator as an inorganic sulfate on the SO_x capturing oxide follows. The step of reducing the inorganic sulfate to a sulfide in a fluid particle bed reactor/stripper follows. Then, releasing the sulfur as H_2S upon hydrolysis in the stripper.

The invention also includes a process for preparing a catalyst for the removal of SO_x. This process comprises the step of blending at least one SO_x capturing oxide and at least one inorganic binder in an aqueous solution. Drying the blend of SO_x capturing oxide and inorganic binder follows in a spray dryer to form dried microspheroidal particles of about 90 microns to about 500 microns in diameter.

DETAILED DESCRIPTION OF THE INVENTION

The invention is a catalyst composition having at least one sulfur oxide ("SO_x") capturing oxide and a binder. The preferred SO_x capturing oxide is a composition containing zinc titanate. The invention uses the catalyst composition in a process to reduce the emissions of sulfur compounds from industrial processes such as the fluid cracking catalyst ("FCC") process used in petroleum refineries and the coal gasification processes used by utility companies. The invention is also directed to processes for producing the fluidizable, spheroidal catalysts composition.

The catalyst composition is desirably formed into a fluidizable particle that is useful in both fluid bed and ebullating bed processes. An example of a fluid bed application is the use of the catalyst composition as a fluid cracking catalyst additive used in petroleum

refineries to reduce SO_x emissions from the fluid cracking catalyst regenerator flue gas. An example of an ebullating bed application is the use of the catalyst composition by a utility company to remove H_2S from the flue gas or hot gas that is generated by the coal gasification process.

The SO_x capturing oxide of the invention is desirably a mixed inorganic oxide additive for catalyzing the capture and release of sulfur-containing compounds in the fluid cracking catalyst provides refiners with an effective means for reducing fluid cracking catalyst SO_x emissions. The invention is a catalyst composition for a formed spheroidal catalyst that reduces the emissions of sulfur containing compounds from industrial processes. For example, in the preferred embodiment of this catalyst, a mixed inorganic oxide particle containing zine titanate, the zinc component "captures" and, thereby, removes the sulfur containing species, such as H_2S or SO_x that is present in the gas stream being treated.

The catalyst composition includes a combination of inorganic oxides with an inorganic binder, an organic binder, or a mixture of an inorganic and organic binder. Desirable inorganic oxides include a member selected from the group consisting of oxides or hydroxides of aluminum, calcium, cobalt, copper, iron, magnesium, molybdenum, silicon, titanium, vanadium, zinc, tungsten, strontium, nickel, manganese, zirconium, barium, members of the lanthanide series, and mixtures thereof. A desirable composition has zinc oxide and titanium dioxide in a molar ratio of about 0.8 to 1.5. The preferred zinc titanate catalyst composition also contains between two and five percent bentonite clay.

Many of the inorganic oxides for use with this invention are commercially available. For example, desirable zinc oxide powder for use with this invention

has an average particle size of about 0.12 microns with a surface area of about $9m^2/g$ and is about 99.4 percent pure. Desirable titanium dioxide powder is in the rutile form and has an average particle size of about 0.5 microns with a surface area of about 12m2/g and is about 94 percent pure.

The catalyst composition also includes a binder component to "glue" the inorganic oxides together into the formed spheroidal particles that are the catalyst. Depending on the application, different binding systems are used. For example, in more severe, high temperature applications such as fluid cracking catalyst, a hydrothermally stable inorganic binder such as aluminum chlorohydrol or peptized alumina is used. Effective inorganic binders include sols of aluminum such as aluminum chlorohydrol, peptized aluminas, sols of silica, colloidal silicas, sols of titanium, sols of zirconium, clays such as bentonite, calcined kaolinite, kaolinite, metakaolin, montmorillonite, chlorite, and talc, and mixtures of these. Desirable inorganic binders include at least one member selected from the group consisting of a sol of aluminum, peptized alumina, a sol of silica, colloidal silica, a sol of titanium, a sol of zirconium, a clay, and mixtures thereof. When the inorganic binder includes a clay, the clay is desirably a member selected from the group consisting of a smectite, calcined kaolinite, kaolinite, metakaolin, chlorite, talc, and mixtures of these. The smectite clays are especially desirable alone or in combination with another inorganic binder and a desirable smectite is a member selected from the group consisting of bentonite, montmorillonite, nontronite, hectorite, saponite, and mixtures of these. Desirable concentrations of inorganic binders are from about 2 to about 15 weight percent.

The preferred inorganic binder for the catalyst composition is a mixture. The mixture of inorganic binder

has at least a first inorganic binder and a second inorganic binder. The first inorganic binder is a member selected from the group consisting of a sol of aluminum, peptized alumina, a sol of silica, colloidal silica, a sol of titanium, a sol of zirconium, a calcined kaolinite, kaolinite, metakaolin, chlorite, talc, and mixtures of these. The second inorganic binder is a smectite. The smectite is a member selected from the group consisting of bentonite, montmorillonite, nontronite, hectorite, saponite, and mixtures of these. The preferred concentration ratio of the first inorganic binder to the second inorganic binder is about two-thirds to about one-third.

In some applications such as a fluidized or ebullating bed found in many flue gas desulfurization units, an organic binder such as hydroxypropyl methyl cellulose or polyvinyl alcohol is used. Desirable organic binders include hydroxypropyl methyl cellulose, poly alcohols or mixtures of poly alcohols such as polyvinyl alcohol or polyethylene glycol, polyvinyl acetate, starch, molasses, lignin sulfonate, hydroxypropyl cellulose, and mixtures of these. Desirable concentrations of organic binders are from about 0.1 to about 10 weight percent.

Other components can be added to the catalyst composition to enhance the performance of the catalyst in specific applications or for a specific set of operating conditions. For example, in the fluid cracking catalyst application, the invented catalyst captures the SO_3 component of the regenerator gasses. The rate limiting step in the series of chemical reactions that include this SO_3 capture is the rate of formation of the SO_3 in the fluid cracking catalyst regenerator. An oxidation promoter such as platinum can be added to the catalyst composition to facilitate the oxidation of SO_x to SO_3 in the fluid cracking catalyst regenerator thus improving

the overall performance of the catalyst. Desirable additional components can include any number of activators, promoters, oxidizers, reducers, scavengers, and mixtures of these components. These material do not change the overall catalytic performance or functionality of the catalyst but merely enhance or optimize its performance.

Numerous surfactants can be used in the catalyst composition of this invention as well. A surfactant is initially selected for its stability in the component to which it is added. For example, the surfactant can be added to numerous "streams" that are used in the process of making this catalyst. A stream is often a slurry of a component used to form the desired particle. A stream can also be a dry component. If a stream, within which a surfactant is to be added, is acidic or alkaline, a surfactant must be chosen that is stable in the Ph of the selected stream. The surfactants are used primarily to enhance the manufacturing process when making the catalyst. Surfactants aid in the dispersion of the individual component particles that make up the catalyst and provide for particles that have superior density and hardness characteristics. Desirable surfactants include anionic fluorohydrocarbon materials. A suitable concentration of surfactant is desirably between about 0.25 and about four grams per five kilograms of dried product.

The catalyst composition preferably is in the form of a spheroidal particle of between about one and 10,000 microns in diameter. This spheroidal particle can be formed by spray drying or bead forming operations depending upon the diameter particle that is desired. Spheroidal particles are desirable because of their ability to become fluidized in fluidized or ebullating bed units. The preferred catalyst composition is dried into spheroidal particles in one of two conditions

depending upon its intended use. The conditions include a first condition having an average particle size of between 60 and 80 microns for fluid cracking catalyst operations and a second condition having an average particle size of between 160 and 250 microns for fluid bed or ebulating bed operations. When the catalyst composition is dried into spheroidal particles having an average particle size of between 160 and 250 microns and the extreme particle range is desirably between 90 and 500 microns.

This invention is also the use of a catalyst composition to reduce the emissions of sulfur compounds from industrial processes. In a fluid cracking catalyst process, the catalyst composition is known as an fluid cracking catalyst "additive" and is added to the fluid cracking catalyst unit in the same manner as the cracking catalyst that is being used. The additive can be added separately or together in a mixture with the cracking catalyst. Usually the addition is accomplished by a pneumatic conveying system to blow the material directly into the fluid cracking catalyst generator. The catalyst additive then circulates through the fluid cracking catalyst unit in direct contact and along with the fluid cracking catalyst. The quantity of fluid cracking catalyst additive that is added and which then circulates in the unit must be sufficient to effectively reduce the emissions of sulfur containing compounds from the fluid cracking catalyst unit, yet it must not be present in a proportion so large that it substantially affects the operation of the cracking side of the process. Therefore, an fluid cracking catalyst additive level of between about 0.5 and about 10.0 percent of the circulating fluid cracking catalyst inventory is desirable.

The fluid cracking catalyst additive of this invention reduces the amount of SO_x emissions from a fluid catalytic cracking unit by "capturing" the SO_x in

the fluid cracking catalyst regenerator section and "releasing" this captured sulfur as H_2S in the stripper/reactor sections of the fluid cracking catalyst unit. The additive promotes the oxidation of SO_x to SO_3 in the fluid cracking catalyst regenerator, captures this SO_3 in the fluid cracking catalyst regenerator by forming an inorganic sulfate, and reduces this inorganic sulfate in the fluid cracking catalyst stripper/reactor to H_2S. This H_2S is later removed downstream. In the preferred embodiment of this invention, the zinc titanate component provides the functionality of SO_x capture and H_2S release.

In the coal gasification process, the flue gas or hot gas is passed through a fluidized or ebullating bed of catalyst to remove H_2S. The catalyst "captures" the H_2S by forming an inorganic sulfide in the absorption stage of the process. This inorganic sulfide is then oxidized in the presence of oxygen in the regeneration stage of the process. The catalyst is restored to the original inorganic oxide and SO_x is released which is later removed downstream.

The invention is also directed to processes for producing the catalyst. A first is a spray drying process to make smaller microspheroidal catalyst particles and a second is a beading or tumbling process to make larger spheroidal catalyst particles. As stated previously, the catalyst composition is in the form of a spheroidal particle of between about one and about 10,000 microns in diameter. The process that is selected to be followed depends, therefore, upon the diameter particle that is desired. In general, spheroidal particles are desirable because of their ability to become fluidized in fluidized or ebullating bed units.

The spray drying process begins with the acquisition and preparation of the raw materials. Commercial grades of the inorganic oxides desired are usually readily

available. For example, in the preferred embodiment, zinc oxide and titanium dioxide are available from any number of sources. The inorganic oxide components are dry blended along with any other of the catalyst components that are acquired in dry form such as a clay material. The binder is prepared in a high shear mixer in an aqueous solution or slurry depending upon the binder selected. The mixture of dry blended ingredients is then slowly added to the binder solution to form a homogeneous aqueous slurry. The solids content of this slurry is then adjusted with water to make a suitable spray dryer feed of between about five to about 50 percent solids. The feed is then spray dried to form the microspheroidal catalyst particles. These particles can be further processed by calcination, washing, ion exchange, and/or drying if necessary or desired to improve the catalysts performance characteristics.

If larger spheroidal particles are desired, a beading or tumbling process is used. This process can be used to form particle sizes of about 100 microns to about 10,000 microns and larger. However, even though much larger sizes are possible, these sized beads are not of as much interest for fluid and ebullating bed applications.

First, the binder component is prepared in the form of a dilute aqueous solution. Any number of binders can be used. Next, the commercial grades of the inorganic oxide materials that are desired are dry blended along with any other components that are acquired in dry form, such as a clay material. The dry blend is put into a bead forming machine or tumbler of the kind used commercially to make beads such as a Nauta or Eirich mixer. The dry material is then tumbled while a fine spray of the binder solution is applied to the powder to form the spheroidal particles. Binder solution is applied and the material tumbled until the desired particle size is achieved.

These particles can be further processed by calcination, washing, ion exchange, and/or drying if necessary or desired to improved the catalysts performance characteristics.

EXAMPLES

The following examples represent the catalyst composition as well as the processes of the invention.

EXAMPLE 1

This example represents the preferred embodiment of the invention by forming zinc titanate based particles suitable for use in an fluid cracking catalyst unit. The zinc titanate particles are formed from the inorganic oxide particles of zinc oxide and titanium dioxide.

First, the binder component is prepared. In this example, peptized alumina is being used to bind the catalyst. In a high shear mixer, a solution of 16 percent formic acid is added to a slurry solution of 16 percent pseudoboehmite alumina in water. A 50/50 blend of these two solutions is prepared in quantities sufficient to have 4.1 pounds of dry basis alumina in the blend.

Next, fine commercial grades of zinc oxide and titanium dioxide as described above are dry blended. They are blended to a ratio of one mole of zinc oxide to 1.5 moles of titanium dioxide. This example uses 13.1 pounds of zinc oxide and 8.7 pounds of titanium dioxide. An additional 1.2 pounds of bentonite clay is added to this blend.

The zinc oxide, titanium dioxide, and clay mixture is added slowly to the binder solution in the high shear mixer and is blended. The blending continues under high shear for at least five minutes or until the blend appears homogeneous. The solids level of this slurry blend is then adjusted with water to make a spray dryer feed of about 15 to 20 percent solids.

The blended material is fed to an APV spray dryer with a spinning wheel atomizer. The inlet temperature is about 340°C and the outlet temperature is about 145°C. The spray dryer feed time is 29 minutes. Microspheroidal particles with an average particle size of 70 to 80 microns are formed.

The spray dried particles are then calcined. Calcining is performed at 830°C for one and one-half hours.

EXAMPLE 2

This example produces zinc titanate particles by the process of the invention which are then blended with a combustion promoter.

An amount of nine pounds of the formed particles of example 1 are homogeneously blended with one pound of a commercial CO combustion promoter. The combustion promoter used in this example is alumina oxide impregnated with 500 parts per million of platinum.

EXAMPLE 3

This example produces zinc titanate particles by the process of the invention with a combustion promoter added directly to the formed particles.

Formed zinc titanate particles are produced according to example 1. Ten pounds of these particles are placed in a rotary chamber and sprayed with a stock solution of 20 percent chloroplatinic acid to impregnate the particles. The spraying is performed while the particles tumble in the rotary chamber until a sufficient quantity of chloroplatinic acid is applied to provide 50 parts per million of platinum to the formed particles. The particles are then dried to remove any excessive moisture.

EXAMPLE 4

This example is another embodiment of the invention wherein the zinc titanate particles that are produced are of a larger particle size suitable for use in a fluidized bed application such as hot gas desulfurization in a coal gasification unit.

As in example 1, first the binder component is prepared. The binder solution used in this example is a dilute solution of 1,410 grams of polyvinyl alcohol, 682 grams of polyethylene glycol, and 100 milliliters of Darvon #7 surfactant in 70 pounds of water.

Next, fine commercial grades of zinc oxide and titanium dioxide are dry blended. As before, they are blended to a ratio of one mole of zinc oxide to 1.5 moles of titanium dioxide. This example uses 15.3 pounds of zinc oxide and 10.2 pounds of titanium dioxide. An additional 1.7 pounds of bentonite clay and 3.5 pounds of kaolin clay are added to this blend.

The zinc oxide, titanium dioxide, and clay mixture is added slowly to the binder solution in the high shear mixer and is blended. The blending continues under high shear for at least five minutes or until the blend appears homogeneous. The solids level of this slurry blend is then adjusted with water to make a spray dryer feed of about 20 to 30 percent solids.

The blended material is fed to an APV spray dryer that has been adapted with a high pressure, single fluid nozzle. Spray dryer conditions are modified so that larger sized particles are produced. In this example, microspheroidal particles with an average particle size of 150 microns are formed.

The particles are then calcined according to example 1.

EXAMPLE 5

This example represents another type of process, a beading process, that can be used to form larger sized spheroidal particles of the catalyst. In this example particle sizes of 100 micron to 10,000 microns are produced; however, much larger sizes are possible, although these sized beads are not of as much interest for fluid and ebullating bed applications.

First, the binder component is prepared. In this example, a stock solution of 0.5 weight percent hydroxypropyl methyl cellulose is mixed. Also, five grams of Zonyl TBS surfactant solution are prepared such that one part of surfactant is diluted with 20 parts of deionized water. The surfactant solution is then added to the hydroxypropyl methyl cellulose solution.

Next, fine commercial grades of zinc oxide and titanium dioxide as described above are dry blended. They are blended to a ratio of one mole of zinc oxide to 1.5 moles of titanium dioxide. This example uses 13.1 pounds of zinc oxide and 8.7 pounds of titanium dioxide. An additional 1.2 pounds of bentonitic clay are added to this blend.

The dry zinc oxide, titanium dioxide, and clay mixture is put into a bead forming machine or tumbler of the kind used commercially to make beads such as a Nauta or Eirich mixer. In this example an LCI granulator is used. The dry material is then tumbled while a fine spray of the binder solution is applied to the powder to form the spheroidal particles. Binder solution is applied and the material tumbled until the desired particle size is achieved.

The particles are then calcined according to example 1.

We claim:

1. A catalyst composition consisting essentially of:

at least one SO_x capturing oxide; and

at least one inorganic binder.

2. The catalyst composition of claim 1 wherein said at least one inorganic binder includes a member selected from the group consisting of a sol of aluminum, peptized alumina, a sol of silica, colloidal silica, a sol of titanium, a sol of zirconium, a clay, and mixtures thereof.

3. The catalyst composition of claim 2 wherein said at least one inorganic binder is a clay, said clay being a member selected from the group consisting of a smectite, calcined kaolinite, kaolinite, metakaolin, chlorite, talc, and mixtures of these.

4. The catalyst composition of claim 3 wherein said smectite is a member selected from the group consisting of bentonite, montmorillonite, nontronite, hectorite, saponite, and mixtures of these.

5. The catalyst composition of claim 2 wherein said at least one inorganic binder includes at least a first inorganic binder and a second inorganic binder,

said first inorganic binder being member selected from the group consisting of a sol of aluminum, peptized alumina, a sol of silica, colloidal silica, a sol of titanium, a sol of zirconium, a calcined kaolinite, kaolinite, metakaolin,chlorite, talc, and mixtures of these and

said second inorganic binder is a smectite, said smectite being a member selected from the group consisting of bentonite, montmorillonite, nontronite, hectorite, saponite, and mixtures of these.

6. The catalyst composition of claim 5 wherein said inorganic binder includes only said first inorganic binder and said second inorganic binder, and a concentration ratio of said first inorganic binder to said second inorganic binder is about two-thirds to about one-third.

7. The catalyst composition of claim 1 wherein said wherein said at least one SO_x capturing oxide is an inorganic oxide being a member selected from the group consisting of oxides or hydroxides of aluminum, calcium, cobalt, copper, iron, magnesium, molybdenum, silicon, titanium, vanadium, zinc, tungsten, strontium, nickel, manganese, zirconium, barium, members of the lanthanide series, and mixtures thereof.

8. The catalyst composition of claim 6 wherein said composition is dried into spheroidal particles in one of two conditions, said conditions being:

a first condition having an average particle size of between 60 and 80 microns; and

a second condition having an average particle size of between 160 and 250 microns.

9. The catalyst composition of claim 8 wherein said composition is dried into spheroidal particles having an average particle size of between 160 and 250 microns and an extreme particle range of between 90 and 500 microns.

10. A catalyst composition consisting essentially of:

a SO_x capturing oxide; and

at least one inorganic binder, said at least one inorganic binding includes a smectite clay.

11. The catalyst composition of claim 10 wherein said smectite clay is a member selected from the group consisting of bentonite, montmorillonite, nontronite, hectorite, saponice, and mixtures of these.

12. The catalyst composition of claim 11 wherein said inorganic binder further includes a member selected from the group consisting of a sol of aluminum, peptized alumina, a sol of silica, colloidal silica, a sol of titanium, a sol of zirconium,and mixtures thereof.

13. The catalyst composition of claim 12 wherein said inorganic binder is up to about 20 percent of an inorganic binder mixture, said inorganic binder mixture contains about two-thirds binder to one-third smectite clay.

14. A catalyst composition consisting essentially of:

a SO_x capturing oxide;

up to about 20 percent of an inorganic binder mixture, said inorganic binder mixture containing about two-thirds binder to one-third smectite clay; and

an organic binder.

15. The catalyst composition of claim 14 wherein said organic binder includes a member selected from the group consisting of hydroxypropyl methyl cellulose, poly alcohols, polyvinyl acetate, starch, molasses, lignin sulfonate, hydroxypropyl cellulose, polyethylene glycol, and mixtures thereof.

16. The catalyst composition of claim 15 wherein said organic binder is a mixture of polyvinyl alcohol and polyethylene glycol.

17. The catalyst composition of claim 14 wherein said at least one inorganic binder includes a member selected from the group consisting of a sol of aluminum, peptized alumina, a sol of silica, colloidal silica, a sol of titanium, a sol of zirconium, a clay, and mixtures thereof.

18. The catalyst composition of claim 17 wherein said at least one inorganic binder is a clay, said clay being a member selected from the group consisting of a smectite, calcined kaolinite, kaolinite, metakaolin, chlorite, talc, and mixtures of these.

19. The catalyst composition of claim 18 wherein said smectite is a member selected from the group consisting of bentonite, montmorillonite, nontronite, hectorite, saponite, and mixtures of these.

20. The catalyst composition of claim 17 wherein said at least one inorganic binder includes at least a first inorganic binder and a second inorganic binder,

said first inorganic binder being member selected from the group consisting of a sol of aluminum, peptized alumina, a sol of silica, colloidal silica, a sol of titanium, a sol of zirconium, a calcined kaolinite, kaolinite, metakaolin, chlorite, talc, and mixtures of these and

said second inorganic binder is a smectite, said smectite being a member selected from the group consisting of bentonite, montmorillonite, nontronite, hectorite, saponite, and mixtures of these.

21. The catalyst composition of claim 20 wherein said inorganic binder includes only said first inorganic binder and said second inorganic binder, and a concentration ratio of said first inorganic binder to said second inorganic binder is about two-thirds to about one-third.

22. The catalyst composition of claim 14 wherein said wherein said at least one SO_x capturing oxide is an inorganic oxide being a member selected from the group consisting of oxides or hydroxides of aluminum, calcium, cobalt, copper, iron, magnesium, molybdenum, silicon, titanium, vanadium, zinc, tungsten, strontium, nickel, manganese, zirconium, barium, members of the lanthanide series, and mixtures thereof.

23. The catalyst composition of claim 21 wherein said composition is dried into spheroidal particles in one of two conditions, said conditions being:

a first condition having an average particle size of between 60 and 80 microns; and

a second condition having an average particle size of between 160 and 250 microns.

24. The catalyst composition of claim 23 wherein said composition is dried into spheroidal particles having an average particle size of between 160 and 250 microns and an extreme particle range of between 90 and 500 microns.

25. A catalyst composition consisting essentially of:

a SO_x capturing oxide;

at least one member selected from the group consisting of an activator, a promoter, an oxidizer, a reducer, a scavenger, and mixtures thereof;

up to about 20 percent of an inorganic binder mixture, said inorganic binder mixture containing about two-thirds structural binder to one-third smectite clay; and

an organic binder.

26. A process for reducing the amount of SO_x emissions passing through a fluid particle bed comprising:

introducing into the fluid particle bed a microspheroidal catalyst having a composition comprising:

at least one SO_x capturing oxide and

at least one inorganic binder;

oxidizing on said microspheroidal catalyst SO_x emissions of SO_2 to SO_3 in a fluid particle bed regenerator;

capturing said SO_3 in said fluid particle bed regenerator as an inorganic sulfate on said SO_x capturing oxide; and

reducing said inorganic sulfate to a sulfide in a fluid particle bed reactor/stripper; and

releasing said sulfur as H_2S upon hydrolysis in said stripper.

27. The process of claim 26 wherein said fluid particle bed is a fluid cracking catalyst.

28. The process of claim 26 wherein said fluid particle bed in an ebullating or fluidized bed reactor for a coal gasification unit wherein flue gas or hot gas of said coal gasification unit is passed through said ebullating or fluidized bed.

29. The process of claim 26 wherein said organic binder includes a member selected from the group consisting of hydroxypropyl methyl cellulose, poly

alcohols, polyvinyl acetate, starch, molasses, lignin sulfonate, hydroxypropyl cellulose, polyethylene glycol, and mixtures thereof.

30. The process of claim 29 wherein said organic binder is a mixture of polyvinyl alcohol and polyethylene glycol.

31. The process of claim 26 wherein said at least one inorganic binder includes a member selected from the group consisting of a sol of aluminum, peptized alumina, a sol of silica, colloidal silica, a sol of titanium, a sol of zirconium, a clay, and mixtures thereof.

32. The process of claim 31 wherein said at least one inorganic binder is a clay, said clay being a member selected from the group consisting of a smectite, calcined kaolinite, kaolinite, metakaolin, chlorite, talc, and mixtures of these.

33. The process of claim 32 wherein said smectite is a member selected from the group consisting of bentonite, montmorillonite, nontronite, hectorite, saponite, and mixtures of these.

34. The process of claim 31 wherein said at least one inorganic binder includes at least a first inorganic binder and a second inorganic binder,

said first inorganic binder being member selected from the group consisting of a sol of aluminum, peptized alumina, a sol of silica, colloidal silica, a sol of titanium, a sol of zirconium, a calcined kaolinite, kaolinite, metakaolin, chlorite, talc, and mixtures of these and

said second inorganic binder is a smectite, said smectite being a member selected from the group

consisting of bentonite, montmorillonite; nontronite, hectorite,saponite, and mixtures of these.

35. The process of claim 34 wherein said inorganic binder includes only said first inorganic binder and said second inorganic binder, and a concentration ratio of said first inorganic binder to said second inorganic binder is about two-thirds to about one-third.

36. The process of claim 26 wherein said wherein said at least one SO_x capturing oxide is an inorganic oxide being a member selected from the group consisting of oxides or hydroxides of aluminum, calcium, cobalt, copper, iron, magnesium, molybdenum, silicon, titanium, vanadium, zinc, tungsten, strontium, nickel, manganese, zirconium, barium, members of the lanthanide series, and mixtures thereof.

37. The process of claim 35 wherein said composition is dried into spheroidal particles in one of two conditions, said conditions being:

a first condition having an average particle size of between 60 and 80 microns; and

a second condition having an average particle size of between 160 and 250 microns.

38. The process of claim 37 wherein said composition is dried into spheroidal particles having an average particle size of between 160 and 250 microns and an extreme particle range of between 90 and 500 microns.

39. A process for preparing a catalyst for the removal of SO_x comprising the steps of:

blending at least one SO_x capturing oxide and at least one inorganic binder in an aqueous solution;

drying said blend of SO_x capturing oxide and inorganic binder in a spray dryer to form dried microspheroidal particles of about 90 microns to about 500 microns in diameter.

40. The process of claim 39 wherein said dried particles are calcined at a temperature greater than about 800°C for at least about 1.5 hours.

41. The process of claim 40 wherein said dried particles are produced with an average particle size of 60 to 80 microns.

42. The process of claim 39 wherein one or more of the components of the catalyst are milled.

43. The process of claim 39 wherein said formed particles are contacted with a member selected from the group consisting of water, an ion exchange solution, and mixtures thereof to remove sodium and other cations.

44. The process of claim 39 wherein said contacting is performed in a batch process comprising:

aqueously mixing said formed particles in tanks with at least one of water or an ion exchange solution; and

dewatering said formed particles.

45. The process of claim 39 wherein said contacting is performed in a continuous process comprising:

aqueously mixing said formed particles in tanks with at least one of water or an ion exchange solution;

feeding said formed particles onto a single or multi-zoned horizontal belt filter to form a filter cake;

at least one of washing or contacting with an ion exchanging solution the filter cake in a countercurrent flow where said water and/or ion exchange solution is

introduced onto the top of the filter cake and pulled through the filter cake by vacuum.

46. The process of claim 45 wherein said filter cake is then dried to remove at least one of moisture or ammonia.

47. The process of claim 39 wherein said particles are impregnated with an additive selected from the group consisting of an activator, a promoter, an oxidizer, a reducer, a scavenger,and mixtures thereof.

48. A process for preparing the catalyst of claim 39 comprising the steps of:

dry blending said mixture of inorganic oxides with an inorganic binder, an organic binder, or a mixture of these;

forming said dry blended mixture into spheroidal particles of about 100 microns to about 10,000 microns in diameter in a mixer.

49. The process of claim 48 wherein said formal particles are calcined at a temperature greater than about 800°C for at least about 1.5 hours.

50. The process of claim 49 wherein said formed particles are contacted with least one of water or an ion exchange solution having ammonium to remove sodium or other cations.

51. The process or claim 50 wherein said washing and/or ion exchange is performed in a batch process comprising:

aqueously mixing said formed particles in tanks with at least one of water or the ion exchange solution;

dewatering said formed particles.

52. The process of claim 39 wherein contacting with at least one of or ion exchange solution is performed in a continuous process comprising:

aqueously mixing said formed particles in tanks with water or an ion exchange solution;

feeding said formed particles onto a belt filter to form a filter cake; and

washing or ion exchanging said filter cake in a countercurrent flow.

53. The process of claim 39 wherein said filter cake is then dried to remove at least one of moisture and ammonia.

54. The process of claim 39 wherein said particles are impregnated with an additive selected from the group consisting of an activator, a promoter, an oxidizer, a reducer, a scavenger,and/or mixtures of these.

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A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B01J 23/06; C01B 17/78
US CL :423/244.1, 244.09, 244.11; 502/341, 342, 343, 350
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/244.1, 244.09, 244.11; 502/341, 342, 343, 350

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,495,304 (Yoo et al) 22 January 1985, column 7, lines 50-70, and column 14, lines 35-45.	1-54
Y	US, A, 4,472,267 (Yoo et al) 18 September 1984, columns 9-10.	1-54
Y	US, A, 4,469,589 (Yoo et al) 04 September 1984, column 5, lines 50-70 and column 7, line 50 to column 8, line 45.	1-54
Y	US, A, 4,686,204 (Mester et al) 11 August 1987, column 3, lines 35-40, column 5, lines 35-40 and column 6, line 50-55.	1-54

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
03 DECEMBER 1996	21 JAN 1997

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Nguandra Roy fw GLENN CALDAROLA
Facsimile No. (703) 305-3230	Telephone No. (703) 305-6118